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Analysis of stable isotope ratios of Ba by double-spike standard-sample bracketing using multiple-collector inductively coupled plasma mass spectrometry†

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A precise analytical method in determining stable Ba isotope ratios was developed by applying a ^{130}Ba-^{135}Ba double-spike corrected standard-sample bracketing method with multiple-collector inductively coupled plasma mass spectrometry (MC−ICP−MS). Data were expressed as per mil deviation from a Ba standard in the $\delta^{137/134}$Ba notation. Careful examinations on the temporal instabilities of the instrument and on the ^{130}Xe and ^{134}Xe interferences permitted accurate analysis of $\delta^{137/134}$Ba. The isotopic ratios of the ^{130}Ba-^{135}Ba double-spike used in this study were ^{134}Ba/^{130}Ba = 0.076528, ^{135}Ba/^{130}Ba = 1.060129, and ^{137}Ba/^{130}Ba = 0.209145. These were determined iteratively by measurements of $\delta^{137/134}$Ba in the IAEA-CO-9 standard with different spike–sample mixing ratios in order to achieve an invariant $\delta^{137/134}$Ba value of IAEA-CO-9. The reproducibility of $\delta^{137/134}$Ba of IAEA-CO-9 was ± 0.032‰ (2SD, n = 42), which was about 5 times better than that reported by a previous study. The $\delta^{137/134}$Ba of JB-2, JA-2, and BHVO-2 igneous rock standard reference materials were 0.086 ± 0.016‰ (2SD, n = 6), 0.016 ± 0.034‰ (2SD, n = 7), and 0.058 ± 0.019 (2SD, n = 5), respectively. A significant difference was observed between the JB-2 and JA-2 results, whereas no significant difference was observed for BHVO-2. These results show that the improved precision opens up a possibility to use $\delta^{137/134}$Ba as a tracer in igneous processes.

(216 words in abstract)

Introduction

Barium (Ba) is a large ion lithophile (LIL) element and that is usually incompatible in mantle rocks.[1] Barium is mobile in fluids and thus an important tracer of fluid circulation in the Earth's interior (*e.g.* Rollinson[2]). Barium abundance in the arc magmas has been used as a sensitive tracer of subducted fluid.[1] Barium is abundant in marine sediments and its stable isotopes may fractionate in the surface environment as shown by the experimental results of von Allmen *et al.*[3] Therefore, Ba isotope ratios should provide a clue to understanding the behaviours of the sediment derived fluids/melts beneath subduction zones.

Barium has seven stable isotopes, which are ^{130}Ba (0.1058% isotopic abundance), ^{132}Ba (0.1012), ^{134}Ba (2.417), ^{135}Ba (6.592), ^{136}Ba (7.853), ^{137}Ba (11.232), and ^{138}Ba (71.699).[4] Since the pioneering work of Nier,[5] the isotopic composition of Ba has been measured in several studies (*e.g.* von Allmen *et al.*;[3] Eugster *et al.*;[4] McCulloch and Wasserburg;[6] Hidaka *et al.*;[7,8] Ranen and Jacobsen;[9] Andreasen and Sharma;[10] Hidaka and Gauthier-Lafaye[11]). Eugster *et al.*[4] were the first to apply the double-spike procedure to Ba isotopes.

Fractionation of Ba isotopes may occur in cation exchange column chromatography during Ba separation. Kondoh and Oi[12] observed that the lighter isotopes are depleted in the first cut on the cation exchange column (up to 30 per mil on ^{130}Ba/^{138}Ba). The major advantage of the double-spike technique is that the isotope fractionation that occurs during the chemical separation can be corrected.[13] Therefore, it is not necessary to recover Ba to 100% if isotopic equilibration of the double-spike is achieved in the sample.

The main target of the previous studies has been on nucleogenic Ba isotope anomalies in extraterrestrial materials or in natural fission reactors. Studies on Ba stable isotope fractionation of terrestrial material are scarce. Of these, von Allmen *et al.*[3] developed a high precision analytical method using multiple-collector inductively-coupled plasma mass spectrometry

(MC−ICP−MS) using a ^{130}Ba-^{135}Ba double-spike technique with an achievable reproducibility of ± 0.15‰ (2SD: 2 standard deviations) in $\delta^{137}Ba/^{134}Ba = [(^{137}Ba/^{134}Ba_{sample}) / (^{137}Ba/^{134}Ba_{standard}) - 1] \times 1000$. They found that the marine and the diagenetic barites were depleted in heavy isotope down to -0.5‰ relative to a Ba nitrate standard solution.

In this study, we applied the same double-spike MC−ICP−MS technique while examining carefully the instrumental setup and measurement conditions, especially regarding the temporal instabilities from the instrument and from ^{130}Xe (4.1% isotopic abundance) and ^{134}Xe (10.4) interferences. Here, we report: (a) a revised analytical method for improved reproducibility and (b) confirmed isotopic fractionation of Ba stable isotopes in igneous rock reference samples provided by the Geological Survey of Japan (GSJ) and by the United States Geological Survey (USGS). These results may open up a new field for the application of non-conventional stable isotopes of Ba toward the study of igneous processes.

Reagents, spike, and isotope standard materials

TAMAPURE®-AA grade, ultra-pure water, 38% HF, 68% HNO_3, 70% $HClO_4$ (Tama Chemical Co., Ltd.) were used without any additional purification. TAMAPURE®-AA grade ultra-pure water was used only for dilution of the double-spike standard. De-ionized water and HCl were purified via a two-bottle Teflon® still from Milli-Q® water (Millipore®) and EL grade HCl (Kanto Chemical Co., Inc.), respectively. The ^{130}Ba-enriched spike (enrichment 35.8%, carbonate) and ^{135}Ba-enriched spike (enrichment 93.4%, carbonate) were obtained from the Oak Ridge National Laboratory (ORNL), USA. A Ba standard solution (1000 mg L^{-1} Ba in nitric acid) from Fluka Aldrich was diluted to 50 µg L^{-1} with 0.5 M HNO_3 and it was used for external standardization by standard-sample bracketing in mass spectrometry. An international reference

material of Ba carbonate (IAEA-CO-9, No. 222), which was dissolved and diluted to 50 μg L^{-1} with 0.5 M HNO_3, was analyzed throughout this study to obtain $\delta^{137}Ba/^{134}Ba$ by normalization to this standard.[3]

Sample

Two GSJ rock reference samples (JB-2 and JA-2) and one USGS rock reference sample (BHVO-2) were analyzed in this study. JB-2 is basalt that erupted in 1950–1951 from the Izu-Oshima volcano and has a Ba concentration of 222 μg g^{-1}.[14] JA-2 is high-Mg olivine andesite (sanukitoid) that contains 321 μg g^{-1} Ba.[14] BHVO-2 is basalt from the Kilauea volcano, Hawaii, which contains 130 μg g^{-1} Ba.[15]

Sample preparation

All chemical procedures were performed in a class 100 clean room. Ten to twenty mg of the rock reference samples were decomposed in closed 7 mL Teflon® perfluoroalkoxy (PFA) screw cap vials (Savillex®) with a 1:4 mixture of 12 M $HClO_4$ and 20 M HF, followed by digestion in a 1:4 mixture of 2 M $HClO_4$ and 6 M HCl and then 6 M HCl alone. Finally, the samples were dissolved in 1 mL of 2.5 M HCl. Five to seven aliquots of powders were prepared and decomposed separately for each rock reference sample.

A 1 mL aliquot of cation exchange resin (AG50W-X8, 200–400 mesh, Bio-Rad Laboratories, USA) was loaded into a polypropylene column with a polyethylene filter (Muromac® Mini-Column S; inside diameter 5.0−5.5 mm, length 50 mm). The resin was serially cleaned with 7 mL of 1 M HF, 7 mL of 6 M HCl, and 7 mL of distilled water, before a final clean-up with 1 mL of 2.5 M HCl. The dissolved rock sample solution was then loaded into the prepared

column. The column separation procedure used in this study was similar to the Rb + Sr and rare earth element (REE) + Ba separation procedure described by Takahashi *et al.*[16] where the Ba with the REE fraction was eluted by 5.5 mL of 6 M HCl after removal of major matrixes and Rb + Sr by an 8.5 mL aliquot of 2.5 M HCl. However, instead of 5.5 mL of 6 M HCl, we used 7.0 mL of 1.5 M HNO_3 for the separation of Ba from REE, because the Kd values of REEs in HNO_3 are higher than those of Ba.[17] The column separation described above was conducted with the fully automated open-column chemical-separation system "COLUMNSPIDER."[18] The total procedural blank of Ba was <13 pg.

Mass spectrometry

Instrumental setup

Barium isotope ratios were determined by a Thermo Scientific NEPTUNE MC−ICP−MS (Bremen, Germany), which was fitted with a modified ion sampling interface that included a high-efficiency rotary vacuum pump (E2M80, Edwards, Crawley, West Sussex, UK). This allowed for a higher vacuum of ~1.5 mbar (1 bar = 10^5 Pa) at the expansion chamber.[19] The ion interface cones used were Normal-sampling and X-skimmer cones (Thermo Fisher, Bremen, Germany). The guard electrode (GE) was kept on (electrically connected) during the analyses. The modifications improved the instrument sensitivity by 800 V ppm^{-1} Ba (= ~50 Gcps ppm^{-1}) using an Aridus II desolvating nebulizer (CETAC Technologies, Omaha, NE, U.S.A.) from which 3–5 mL min^{-1} of additional N_2 gas was introduced. Collector configurations and details of other instrumental parameters are summarized in Table 1. Four isotopes (^{130}Ba, ^{134}Ba, ^{135}Ba, and ^{137}Ba) were selected to calculate $^{137}Ba/^{134}Ba$ using the ^{130}Ba-^{135}Ba double-spike method. Three isotopes (^{132}Ba, ^{136}Ba, and ^{138}Ba) were excluded from this technique owing to the large isobaric

interference of ^{132}Xe (26.9%) on ^{132}Ba (0.1%) and interferences of La and Ce on ^{136}Ba and ^{138}Ba. ^{134}Ba is interfered by ^{134}Xe. The ^{131}Xe peak was monitored throughout the analyses to evaluate the interference and intensity used for overlap correction of ^{134}Xe on ^{134}Ba (see below for Xe baselines).

Standard bracketing for correction of mass-independent fractionation

We applied the standard-sample bracketing method in conjunction with the double-spike technique for MC−ICP−MS in this study. Non-linear mass-dependent fractionation is known to occur when (1) a high-sensitivity skimmer cone, (2) the combination of an X-skimmer cone with a Jet sample cone, or (3) a shield torch (GE) is used.[20,21,22,23] Newman *et al.*[20] reported the occurrence of non-linear mass-independent fractionation for neodymium (Nd) and cerium (Ce) isotopes and proposed that this originated from the isotope-dependent formation of MO^+ *via* an energy-resonant ion−atom reaction. In particular, it was assumed that this occurred at the surface of the skimmer cone. Newman *et al.*[20] also showed that the mass bias in Nd isotope ratios (<0.050‰) can be reduced by adjusting the NdO^+/Nd^+ ratio (<0.1%) through the addition of small quantities of admixed N_2 to the sample gas flow in their Nu Plasma MC−ICP−MS. Furthermore, Newman *et al.*[21] reported the occurrence of non-linear mass-dependent fractionation using the Thermo NEPTUNE MC−ICP−MS and concluded that, even when the formation of NdO^+ is minimized by adjustment of the plasma operating conditions, the exponential law cannot correct for instrumental mass fractionation with the X-skimmer cone geometry.

More recently, Schulz *et al.*[23] presented anomalous results in tungsten (W) isotope measurement using a Jet interface cone in high-resolution mode, although anomalies were not observed in the medium- and low-resolution modes. The authors adopted a standard normal

(N)-sampler cone with an X-skimmer cone for W isotope measurement. Kimura *et al.*[22] further examined various combinations of the N-sampler and normal(N)/X-skimmer cones and GE on−off modes in Thermo NEPTUNE MC−ICP−MS for Nd isotope analyses. They concluded that use of the X-skimmer cone and GE improved instrumental sensitivity but led to increases in NdO^+, which resulted in mass-independent fractionation (see their ESI Data 1, Fig. 1). In particular, they used N-sampler and N-skimmer cones with GE off combined with an improved vacuum at the interface; this setup yielded $NdO^+/Nd^+ < 0.01\%$.

The nature of such anomalous behavior in MC−ICP−MS is currently the subject of intensive study, although it appears to be limited to particular elements. Newman *et al.*[20] confirmed that isotopic data for their hafnium (Hf) and lead (Pb) standards agreed with the reference values within measurement precision, even when a high-sensitivity skimmer cone was used. They also evaluated the mass fractionation corrections for X-skimmer cone geometry using standard-sample bracketing for lithium (Li), silica (Si), and iron (Fe) and found them to be comparable to those for the N-skimmer geometry. External corrections (*e.g.*, standard bracketing or β-correction) have provided accurate Nd isotope ratios, despite the fact that the oxide yield causes a non-linear mass bias in Nd isotope analysis.[24,25,26] Additionally, we have confirmed the validity of the standard bracketing method for strontium (Sr), Nd, Hf, and Pb isotopes at our laboratory, where an X-skimmer cone is used regularly with GE on.

It is possible that anomalous fractionation also occurs in Ba isotope measurements. However, the instrumental setup used here (N-sample X-skimmer cones with GE on) with Aridus II and additional N_2 yielded low BaO/Ba (<0.1%). This should prevent the occurrence of considerable isotopic fractionation. Nevertheless, we applied the standard-sample bracketing method (*e.g.*, Baker *et al.*[27]) to correct for instrumental mass bias after conducting double-spike correction. Theoretically, this approach should eliminate the mass bias entirely. The role of this external

correction will be reviewed in the discussion of the results of Fluka standard analyses.

Calibration of Ba double-spike

Previous calibration method

Normally, a double-spike is calibrated relative to the standard whose isotope ratios are well known. For example, the ^{207}Pb-^{204}Pb double-spike for Pb isotope analysis is calibrated relative to the NIST SRM 982 standard (*e.g.* Miyazaki *et al.*[28]). In this case, Pb isotope ratios of SRM 982 have been analysed independently and reference Pb isotope ratios can be used in order to correct for instrumental isotopic fractionation with thermal ionization mass spectrometry (TIMS) (*e.g.* Todt *et al.*[29]). Conversely, von Allmen *et al.*[3] calibrated their ^{130}Ba-^{135}Ba double-spike relative to a Nd standard solution that has an isotopic composition that is well known. In their method, the instrumental fractionation factor of MC−ICP−MS was determined by ^{142}Nd/^{144}Nd using the Nd standard, and the fractionation factor was applied to correct for the ^{137}Ba/^{135}Ba of a pure standard and the pure spikes. However, the fractionation factor determined by ^{142}Nd/^{144}Nd is different from that for ^{137}Ba/^{135}Ba because of either the space charge effect on the MC−ICP−MS at the ion sampling interface[30] or non-mass dependent fractionation of Nd isotopes (*e.g.* Newman[21]).

Problems in empirical spike calibration

The ^{130}Ba-^{135}Ba double-spike composition and the spike/sample mixing ratio were determined based on the simulation method reported by Rudge *et al.*[31] ^{130}Ba-enriched and ^{135}Ba-enriched spikes were dissolved separately in 0.5 M HNO_3. Then, the single spike solutions of ^{130}Ba and ^{135}Ba were mixed and diluted to approximately 1 mg L^{-1} concentration. However, we cannot determine accurate isotope compositions for a sample without knowing the accurate isotope

compositions of the double-spike.

For this study, we applied the following method for accurate determination of Ba isotope ratios using a double-spike. Isotope ratios of a standard and an unknown sample determined by a common double-spike can provide an accurate isotope composition when δ-notation is used. It is true even if the double-spike is not completely calibrated. For this purpose, we can use the provisional weight data of each Ba spike and the mixing rate between the two spikes. In other words, the errors are on the isotopic mixing lines of the two spikes and are equally relevant to a standard and an unknown sample, providing that there is no procedural contamination of Ba from chemical regents used. However, a problem still persists as shown below.

Although accurate $\delta^{137/134}$Ba can be measured by analysing a standard and a sample with the same double-spike, the analytical errors in the double-spike analyses are propagated from both the mixing ratio between spikes in the double-spike and the mixing ratios between the standard double-spike and the sample double-spike.[31] Figure 1 shows simulation results for propagated errors (shown in ‰, see legend of Figure 1) in measured $\delta^{137/134}$Ba of an unknown sample calculated by using isotope ratios of ^{134}Ba/^{130}Ba, ^{135}Ba/^{130}Ba, and ^{137}Ba/^{130}Ba normalized to a standard.

In Figure 1, we assumed that the mixing ratio of the spike–standard was 0.178 for simplicity. This is reasonable because the Fluka Aldrich Ba standard and the ORNL double-spike can be mixed accurately as they have known concentrations. Then, the spike–sample mixing ratio was intentionally varied from 0.178 (Figure 1, Y-axis) and the double-spike isotope ratios represented by ^{135}Ba/^{130}Ba were also intentionally varied from an assumed true value of 1.60129 (X-axis of Figure 1). The simulations show that at least one of the following factors will be essential: (1) a precisely calibrated double-spike or (2) an accurate spike–sample mixing to obtain the precise $\delta^{137/134}$Ba content of an unknown sample.

If we do not know the accurate double-spike isotope ratios, we must adjust the spike–sample mixing ratio (of Ba) the same as that for the spike–standard (in this case 0.178). However, it was not realistic to accurately adjust the spike–sample mixing ratio because we do not always know the Ba concentration in a sample. The above examinations indicate that an accurately calibrated double-spike is practically needed even if δ-notation is employed.

Method

As described above, the true double-spike isotopic composition is on the mixing line of the two spikes. We applied the following spike calibration method using Fluka Aldrich as the standard and IAEA-CO-9 as the sample. The method used was as follows:

(1) Several mixtures with different spike–sample mixing ratios were measured with a fixed spike–standard mixing ratio.
(2) $\delta^{137/134}$Ba of the sample was calculated using different spike ratios.
(3) ^{134}Ba/^{130}Ba, ^{135}Ba/^{130}Ba, and ^{137}Ba/^{130}Ba of the spike were determined iteratively to achieve an invariant value for all of the measured $\delta^{137/134}$Ba.

Figure 2 shows the result for the calibration of the Ba double-spike by the method described above. Nine mixtures with different spike–sample mixing ratios ranging from 0.11 to 0.33 (actual ^{130}Ba/^{137}Ba in the mixtures was 0.25–0.64) were measured. The double-spike Ba standard mixture was fixed at 0.175 (^{130}Ba/^{137}Ba = 0.35–0.36). The calculated $\delta^{137/134}$Ba of the sample was 0.019 ± 0.058‰ (n = 9) when the Ba isotope ratios in the double-spike were ^{134}Ba/^{130}Ba = 0.076528, ^{135}Ba/^{130}Ba =1.060129, and ^{137}Ba/^{130}Ba = 0.209145.

The calculated $\delta^{137/134}$Ba value using the double-spike isotope ratios determined by the weight data described on the vials by ORNL (i.e., ^{134}Ba/^{130}Ba = 0.076432, ^{135}Ba/^{130}Ba = 1.040925,

244 $^{137}Ba/^{130}Ba$ = 0.208963) was -0.015 ± 0.215‰ (n = 9), which had a larger range of $\delta^{137/134}Ba$
245 values than those estimated by the calibrated double-spike. Thus, we used the calibrated
246 double-spike values for the remaining analyses in this study.
247

248 ## Analytical protocols

249 **On-peak background subtraction and isobaric overlap correction of Xe**

250 The Ar gas used for ICP contained Xe impurities. Barium memories were also present because
251 of residuals in the Aridus II desolvating nebulizer. We subtracted these blanks using on-peak
252 background measurements for about 1 min prior to every analytical run. The ^{130}Xe and ^{134}Xe
253 blank on ^{130}Ba and ^{134}Ba were subtracted using this method. However, Xe signals were not
254 stable even for one single analytical run and this was especially true for a few hours after
255 starting the plasma.

256 Figure 3 illustrates how much of the ^{134}Xe + ^{134}Ba beam is occupied by the ^{134}Xe beam for ~5 h
257 after starting the plasma. The ^{134}Xe signal is normalized to the 0.93 V of the ^{134}Ba signal,
258 assuming the smallest barium beam used in our study (^{130}Ba = 1.57 V, ^{134}Ba = 0.93 V).
259 Although the profiles of each day differ, the ^{134}Xe beam occupied up to 4% of the ^{134}Xe + ^{134}Ba
260 beam. In contrast, the ^{130}Xe beam occupied up to 0.9% of the ^{130}Xe + ^{130}Ba beam. These results
261 demonstrate that it is important to stabilize Xe baselines for Ba isotope measurements. The
262 observations show that Xe signals were unstable and decreased for ~4 h before stabilizing
263 (Figure 3). The contributions of Xe on Ba after 4 h were as follows: $^{130}Xe/(^{130}Xe + ^{130}Ba)$ <
264 0.2% and $^{134}Xe/(^{134}Xe + ^{134}Ba)$ < 0.6%. Although we do not yet know the reason for this
265 instability, it most likely originates from Aridus II, which uses a membrane filter. Therefore, in
266 the present study, we pre-treated the MC−ICP−MS for at least for 4 h before analysis.

Small but significant short-term instabilities of Xe signals continued even after 4 h. The instability influenced the baselines of ^{130}Ba and ^{134}Ba after on-peak background subtraction so additional corrections were necessary. We corrected the ^{130}Xe and ^{134}Xe overlaps using simultaneously measured signals of ^{131}Xe. The ^{130}Xe/^{131}Xe and ^{134}Xe/^{131}Xe ratios, which were necessary to calculate ^{130}Xe and ^{134}Xe intensities, were determined by using defocus baseline measurements. In these measurements, ^{130}Ba and ^{134}Ba blanks from instrumental memories interfered and Ba interference correction was also necessary. The ^{130}Ba and ^{134}Ba intensities were calculated from simultaneously measured ^{135}Ba and ^{137}Ba. The ^{130}Ba/^{137}Ba and ^{134}Ba/^{137}Ba ratios were calculated using exponential mass fractionation correction from ^{135}Ba/^{137}Ba. The fractionation factor for Ba isotopes was determined by comparison to the IUPAC abundances of ^{135}Ba/^{137}Ba = 0.586896.[32]

We determined the values for ^{130}Xe/^{131}Xe and ^{134}Xe/^{131}Xe to be 0.192476 ± 0.000059 (2SE, n = 144) and 0.504815 ± 0.000065 (2SE, n = 142), respectively. The average intensities were ^{130}Xe = 2.5 mV, ^{131}Xe = 13 mV, and ^{134}Xe = 6.7 mV, with ^{130}Ba/^{130}Xe and ^{134}Ba/^{134}Xe determined to be 0.000964 ± 0.000032 (2SE, n = 146) and 0.005997 ± 0.000154 (2SE, n = 146), respectively. These values remained stable over a few months, even for different Ar gas bottles, different interface cones, and different tuning conditions.

It is difficult to propagate the uncertainties of ^{130}Xe/^{131}Xe and ^{134}Xe/^{131}Xe ratios to the calculated ^{137}Ba/^{134}Ba ratios, particularly because the equations of error propagation are complex for the double-spike standard-sample bracketing method. Therefore, we simply estimated these uncertainties by calculating ^{137}Ba/^{134}Ba ratios using ^{130}Xe/^{131}Xe and ^{134}Xe/^{131}Xe ratios that fluctuated between their error ranges. With the exception of one measurement (-0.004 V), the instability of ^{131}Xe after on-peak background subtraction was less than ±0.002 V for all measurements obtained in our laboratory. The deviations of the calculated ^{137}Ba/^{134}Ba ratios

were less than 0.00014‰. In fact, the deviation of the $^{137}Ba/^{134}Ba$ ratios was only 0.00031‰, even when the error of ^{131}Xe was -0.004 V. These deviations were so small relative to the analytical errors of the $^{137}Ba/^{134}Ba$ ratio in replicate analyses (see below) that we considered them to be negligible.

Note that the $^{130}Xe/^{131}Xe$ and $^{134}Xe/^{131}Xe$ values were not corrected for isotopic fractionation, as we monitored only ^{131}Xe. However, this method proved to be useful, as will be demonstrated by the analytical results below.

Data reduction in double-spike standard-sample bracketing method

In this study, we have assumed that both instrumental and natural mass-dependent fractionation follow an exponential law. The three-dimensional data reduction procedure of Siebert *et al.*[13] was applied. $^{134}Ba/^{130}Ba$, $^{135}Ba/^{130}Ba$, and $^{137}Ba/^{130}Ba$ ratios of 100 raw scan data were used for regression calculations on an Excel spreadsheet to obtain corrected $^{137}Ba/^{134}Ba$ ratios by the double-spike method. No further error propagation calculations have to be applied to the bulk errors in the final $^{137}Ba/^{134}Ba$ from samples and standards because the double-spike corrected $^{137}Ba/^{134}Ba$ was calculated for each individual scan data from a single set of $^{134}Ba/^{130}Ba$, $^{135}Ba/^{130}Ba$, and $^{137}Ba/^{130}Ba$ isotope ratios. Then 2SE (2SE: 2 standard errors) were determined based on the 100 individual ratios.

The $^{137}Ba/^{134}Ba$ ratio of the Fluka Aldrich Ba standard solution determined by the double-spike method during this study was 4.56803 ± 0.00037 (2SD, n = 130). The error of the $^{137}Ba/^{134}Ba$ ratio (0.04‰ RSD: relative standard deviation) may be from the non-linear mass-independent instrumental fractionation in the MC−ICP−MS (*e.g.* Newman *et al.*;[20,21] Kimura *et al.*[22]; Schulz *et al.*[23]; also see Mass Spectrometry chapter above), which cannot be corrected for by the double-spike method. Therefore, we used an additional standard-sample

bracketing method after the calculation of the $^{137}Ba/^{134}Ba$ ratio by the double-spike method.

The calculated $^{137}Ba/^{134}Ba$ of the unknown samples was finally given as $\delta^{137/134}Ba$ normalized to the Fluka Aldrich Ba standard, which was measured both before and after the samples. Error propagation calculations were applied using the errors of two bracketing standards and a bracketed sample by Kragten.[33]

Analytical results

Reproducibility of $\delta^{137/134}Ba$ in standards

The reproducibility of $\delta^{137/134}Ba$ was assessed by repeated analyses of the Fluka Aldrich standard solution. The spike–standard mixed solution was measured as samples. The resultant $\delta^{137/134}Ba$ of Fluka Aldrich was 0.000 ± 0.032‰ (2SD, n = 42) (Table 2, Figure 4). The reproducibility of our measurements was about five times better than that of standard measurements by von Allmen *et al.*[3] They also used the Ba standard solution provided from Fluka Aldrich and found a value of 0.00 ± 0.15‰ (2SD, n = 55).

If Ba concentrations of samples are known advance, we can adjust the spike–sample mixing ratio to that of the spike–standard (0.175 in this study). This is effective for obtaining a high reproducibility for unknown samples. We can evaluate this effect by using our results on IAEA-CO-9 (Table 2). The $\delta^{137/134}Ba$ of IAEA-CO-9 measured by different spike–sample mixing ratios of 0.11–0.33 was 0.019 ± 0.058‰ (n = 9). The $\delta^{137/134}Ba$ measured by an optimal spike–sample mixing ratio was 0.034 ± 0.021‰ (2SD, n = 6). Our IAEA-CO-9 results were within the errors measured by von Allmen *et al.*[3] (-0.03 ± 0.06‰ (2SD, n = 4). The reproducibility was about three times better than that by von Allmen *et al.*[3] Although the measurements carried out by different spike–sample mixing ratios showed reproducibility (±

0.058‰) similar to that of von Allmen *et al.*[3] (± 0.06‰), pre-determination of Ba contents in an unknown sample is recommended for better reproducibility. Barium is easily measured either by X-ray fluorescence spectrometry or by Quadrupole ICP−MS.

Fractionation of Ba isotopes in cation exchange column chromatography

Wakaki and Tanaka[34] showed in their Nd isotope experiment that isotope fractionation during column chromatography follows equilibrium isotope fractionation rather than exponential law, although the difference was well within the analytical uncertainty because of their high Nd yield (98.8 ± 0.79%). If this is true, additional correction or ~100% recovery of the yield may be necessary because exponential law is used in the double-spike calculations.

In order to assess the effects of isotopic fractionation during column separation, we passed several aliquots of IAEA-CO-9 through an ion-exchange column before spiking and measured it with the double-spike mixed after separations. The $\delta^{137/134}$Ba of IAEA-CO-9 was 0.022 ± 0.014‰ (2SD, n = 5), which was within the deviation of 0.032 ± 0.018‰ (2SD, n = 5) for the pre-spiked run and 0.034 ± 0.021‰ (2SD, n = 6) without column chemistry. Hence, the effect of isotopic fractionation during column separation was not observed in our study, even though the Ba yield in this study was about 89% on average.

Isotopic compositions of igneous rock reference samples

The measured $\delta^{137/134}$Ba values of two GSJ and one USGS rock reference samples are listed in Table 2. The $\delta^{137/134}$Ba of JB-2, JA-2, and BHVO-2 were 0.086 ± 0.016‰ (2SD, n = 6), 0.016 ± 0.034‰ (2SD, n = 7), and 0.058 ± 0.019‰ (2SD, n = 5), respectively (Figure 5 and Table 2). A significant difference was observed between JB-2 and JA-2, although BHVO-2 was within the deviations of JB-2 and JA-2. The deviation of JA-2 was larger than the deviations of JB-2 and BHVO-2, and was also 1.5 times greater than the deviation of IAEA-CO-9 (0.034 ± 0.019‰)

measured from a common stock solution. The measurements of all rock reference samples were conducted on separate powder aliquots. Therefore, we attribute the larger deviation of JA-2 to natural heterogeneity within the sample.

JB-2 is considered to have originated from fluid fluxed melting of sub-arc mantle peridotite by addition of fluids from subducted sediment and altered oceanic crust at a 50:50 mixing rate.[35] JA-2 is considered to be derived from subducted sediment melt that later interacted with the sub-arc mantle.[36] BHVO-2 is from a Hawaiian hotspot where some recycling component (perhaps pyroxenite of a recycled ocean crust) embedded in a fertile mantle is expected.[37] Among these samples, JA-2 is the most strongly influenced by the Ba-bearing fluid from subducted sediment. While the origin of variation should be explored further, the observation of significant variation between igneous rocks is encouraging because Ba may be useful as a tracer for the subducted sediment component in the sub-arc mantle and arc magmas.

Conclusions

A precise analytical method for determining stable Ba isotopes ($\delta^{137/134}$Ba) was developed using the double-spike corrected standard-sample bracketing method with MC−ICP−MS. In this method, mass-dependent fractionation during chemical separation and mass spectrometry was corrected by the double-spike in addition to a correction for mass-independent fractionation in the MC−ICP−MS by the sample-standard bracketing method. The double-spike was calibrated without a Ba standard by using an iterative calibration method developed in this study. The reproducibility of $\delta^{137/134}$Ba by repeated analyses of a standard solution was about five times better than that reported in a previous study. Using the proposed analytical method, differences in $\delta^{137/134}$Ba for JB-2, JA-2, and BHVO-2 igneous reference rock samples were observed.

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Table 1 Operation parameters for Ba isotope analysis

MC−ICP−MS	Thermo Fisher Scientific, NEPTUNE (modified)
Plasma power	1200 W (27.12 MHz)
Guard electrode	On
Plasma Ar gas flow rate	15 L min^{-1}
Auxiliary Ar gas flow rate	1.00 L min^{-1}
Sample Ar gas flow rate	0.9 L min^{-1}
Sample cone	Normal cone (Ni)
Skimmer cone	X-skimmer cone (Ni)
Interface pump	Pfeiffer UNO35 in tandem with Edwards E2M80 (total = 115 m^3 h^{-1})
Interface vacuum	1.3–1.5 mbar
Mass resolution	M/ΔM = 400 (low resolution)
Typical sensitivity	>800 V ppm^{-1} for Ba using Aridus desolvating nebulizer
Oxide molecular	<0.1% (BaO/Ba by 154/138)
Desolvator	Aridus
Ar sweep gas flow	3.5–3.8 L min^{-1}
N_2 gas flow	3–5 mL min^{-1}
Solution uptake rate	118 μL min^{-1}
Spray chamber temperature	110 °C
Desolvator temperature	160 °C
Detector mode	Faraday cup static mode
	L3 ^{130}Ba 1 × 10^{11} Ω amplifier (Ba signal)
	L2 ^{131}Xe 1 × 10^{11} Ω amplifier (Xe monitor)
	L1 ^{132}Ba 1 × 10^{11} Ω amplifier (Ba signal)
	CF ^{134}Ba 1 × 10^{11} Ω amplifier (Ba signal)
	H1 ^{135}Ba 1 × 10^{11} Ω amplifier (Ba signal)
	H2 ^{136}Ba 1 × 10^{11} Ω amplifier (Ba signal)
	H3 ^{137}Ba 1 × 10^{11} Ω amplifier (Ba signal)
Data acquisition	On-peak background subtraction (60 s before data acquisition)
	Standard bracketing method (Fluka standard)
	100 times, ~8 s scan

Table 2 Results of measurements

Sample	Sample description	Provenance	Ba quantity [µg]	$\delta^{137/134}Ba$	2SD	$^{130}Ba/^{137}Ba$ (not corrected*)	2SD	n
Fluka	Standard solution Aldrich							
Spike/sample = 0.175				0.000	0.032	0.3537	0.0023	42
IAEA-CO-9	Standard ($BaCO_3$)	IAEA						
Spike/sample = 0.11–0.33				0.019	0.058	0.4001	0.2537	9
Spike/sample = 0.175				0.034	0.021	0.3648	0.0027	6
Spiked after column separation, spike/sample = 0.175			0.1	0.022	0.014	0.4044	0.0325	5
Spiked before column separation, spike/sample = 0.175			0.1	0.032	0.018	0.3648	0.0142	5
JB-2	Standard (Basalt)	GSJ						
Spiked before column separation, spike/sample = 0.175			2.3–2.9	0.086	0.016	0.3623	0.0059	6
JA-2	Standard (Andesite)	GSJ						
Spiked before column separation, spike/sample = 0.175			4.3–7.6	0.016	0.034	0.3737	0.0063	7
BHVO2	Standard (Basalt)	USGS						
Spiked before column separation, spike/sample = 0.175			1.4–1.9	0.058	0.019	0.3571	0.0060	5

SD: standard deviation, n: number of measurements, * refers to measured ratio

Figure captions

Fig. 1 Contour plot of the $\delta^{137/134}$Ba value deviation from the correct value of the sample according to the ^{135}Ba/^{130}Ba ratio of double-spike used for calculations or the spike/sample ratio of the measurement mixture for the sample run. The ^{135}Ba/^{130}Ba ratio is on the mixing line of two spikes (^{130}Ba spike and ^{135}Ba spike). The spike/standard ratio of the standard run was fixed to 0.178.

Fig. 2 $\delta^{137/134}$Ba values of IAEA-CO-9 measured with different spike/sample ratios that were calculated by using calibrated and un-calibrated double-spike ratios.

Fig. 3 Examples of ^{134}Xe / (^{134}Xe + ^{134}Ba) ratio (%) showing reduction after plasma start for measurements conducted with the smallest barium beam in our study (^{134}Ba = 0.93 V). The intensity of the ^{134}Xe beam was monitored after plasma start with the ^{134}Ba interference correction in washing solution.

Fig. 4 $\delta^{137/134}$Ba values of the Fluka Aldrich standard solution. The mixed solution of the Fluka Aldrich standard solution and the ^{130}Ba-^{135}Ba double-spike solution used for the bracketing standard were used as samples.

Fig. 5 $\delta^{137/134}$Ba values of JB-2, JA-2, and BHVO-2.

Fig. 1

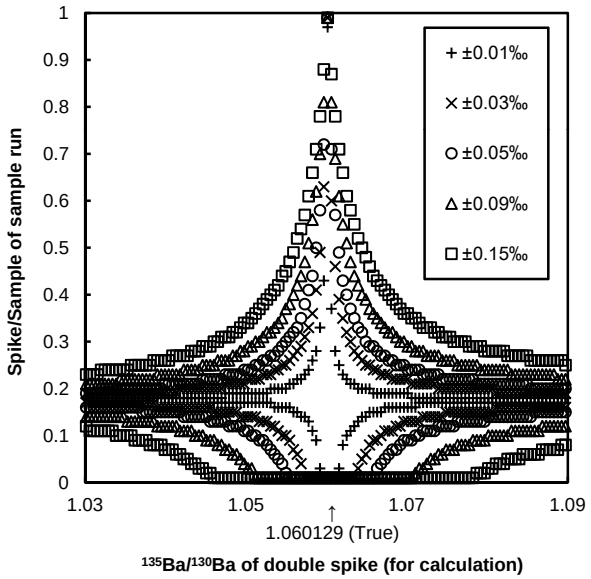
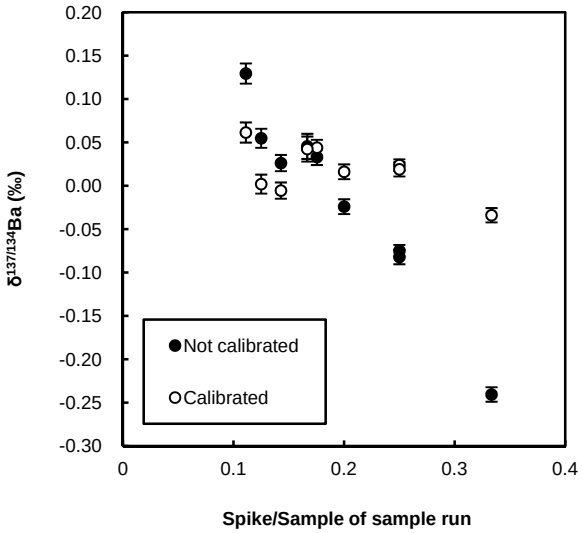

Spike/Sample of sample run
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.03
1.05
1.07
1.09
1.060129 (True)
135Ba/130Ba of double spike (for calculation)
±0.01‰
±0.03‰
±0.05‰
±0.09‰
±0.15‰

Fig. 2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0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
0
0.1
0.2
0.3
0.4
δ137/134Ba (‰)
Spike/Sample of sample run
Not calibrated
Calibrated

Fig. 3

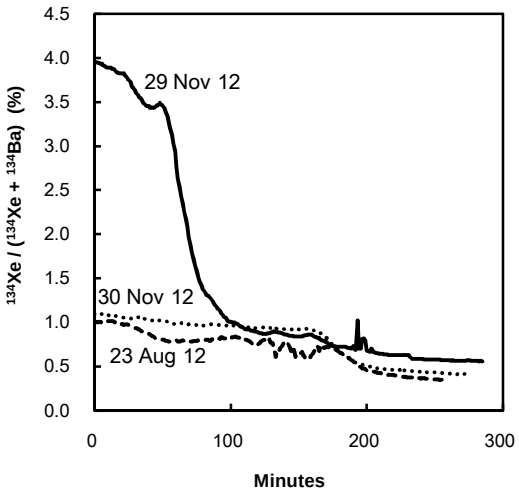

4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
Minutes
^{134}Xe / (^{134}Xe + ^{134}Ba) (%)
29 Nov 12
30 Nov 12
23 Aug 12

Fig. 4

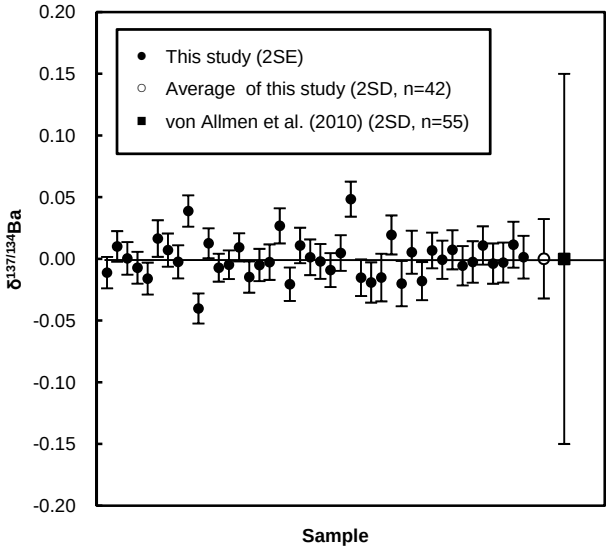
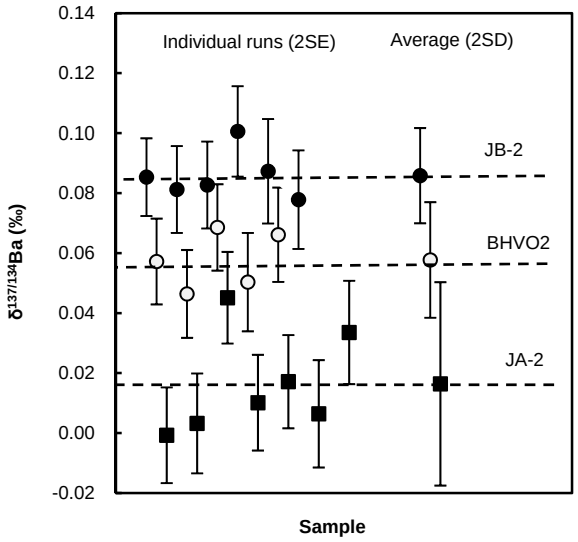

0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
δ137/134Ba
This study (2SE)
Average of this study (2SD, n=42)
von Allmen et al. (2010) (2SD, n=55)
Sample

Fig. 5


Individual runs (2SE)
Average (2SD)
JB-2
BHVO2
JA-2
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
δ137/134Ba (‰)
Sample